

CAPTURING THE CONTORTIONS OF EXCITED MOLECULES

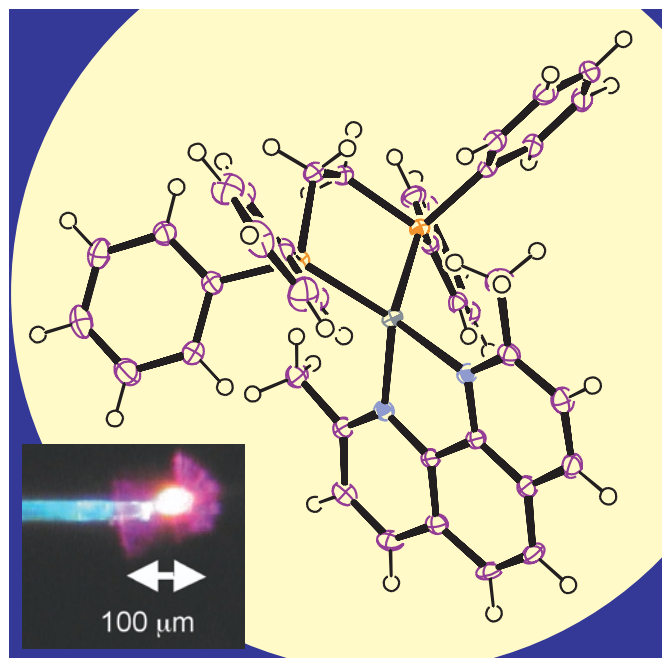
Give a complex molecule a little extra energy, and it tends to get bent out of shape. The structure of an excited molecule may differ from that of the molecule in its ground state, and the distortions can greatly affect the molecule's chemical reactivity and other properties. Reversible shape changes are fleeting, however, lasting only millionths or billionths of a second. To measure them, researchers from the State University of New York at Buffalo and The University of Chicago are developing a technique called "photocrystallography" that essentially provides snapshots of excited molecules within a molecular crystal.

The method adds a new dimension—time—to traditional x-ray crystallography. In a standard technique, monochromatic x-rays diffract off the various planes of symmetry within a slowly rotating single-domain crystal, and the trajectories of the scattered x-rays reveal the arrangement of molecules within the crystal and atoms within the molecules. However, the molecules are generally not excited, and the measurements make no use of timing. Such measurements provide a good long look at the ground state structure of the molecules but yield little insight into the shapes of excited molecules.

To detect reversible shape changes, the researchers hit a molecular crystal with a one-two punch: a nanosecond pulse of intense laser light followed almost immediately by a microsecond burst of x-rays. The pulse of laser light excites many of the molecules in the crystal, and the x-rays diffract off them before they have a chance to relax to their ground state. The deformed molecules alter the intensities of the x-rays diffracted in various directions, and from such intensity changes researchers can deduce the precise shape of the excited molecules. The photons in each laser pulse must outnumber the molecules in the crystal to ensure that a detectable fraction of the molecules—5% to 10%—are excited; the x-rays must be intense enough to determine the crystal structure before the repeated laser pulses damage the crystal. And to keep the laser from vaporizing the tiny sample, the crystal must be cooled with helium gas.

A user facility for time resolved measurements is being commissioned on the ChemMatCARS insertion device beamline at the APS [1]. While preliminary experiments were performed at Brookhaven National Laboratory, ChemMatCARS effort has concentrated on instrumentation development appropriate for a high-brilliance undulator source and data acquisition/analysis packages which promote efficient use of this new capability.

The first experiments at ChemMatCARS used a sample of a photosensitive metalloorganic dye containing a copper atom between phosphorous and nitrogenous ligands. The two ligands are roughly planar and are nearly perpendicular in the molecule's ground state. But when the molecule is excited, an electron hops from the copper to the nitrogenous ligand. That causes the molecule to flatten, the measurements showed, and the angle between the planes of the ligands decreases by several degrees. The distortion was smaller than density functional theory calculations had predicted. However, the calculations had analyzed an



The ground state structure of the photosensitive metalloorganic dye known as $\text{Cu(II)(dmp)(diphos)}^+$. The molecule's excited-state structure was determined by photocrystallography at the APS. Inset: Photograph of laser-illuminated crystal emitting light during photocrystallographic data collection.

isolated molecule, instead of a molecule within a crystal, which would be confined by its neighbors.

These first measurements demonstrate the potential of the technique to capture structural changes caused by any light-induced reversible process. They open the way to myriad applications, and the researchers are hoping that the ChemMatCARS 15-ID beamline can serve as a national user facility for photocrystallography. In the meantime, they are hoping to achieve picosecond x-ray pulses by synchronizing their laser with the circulating particle bunches within the synchrotron. Such x-ray pulses would enable them to resolve even shorter-lived excitation. ○

Reference

[1] P. Coppens, T. Graber, and P.J. Viccaro, *Synchrotron Radiation News* 16 (4), 27-28 (2003)

See: P. Coppens, *Chem. Commun.* **12**, 1317-1320 (2003).

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REFINING THE WAY CATALYSTS ARE MADE

Platinum supported on alumina catalysts are important for production of high-octane gasoline in the petroleum industry and exhaust gas abatement in the automotive industry. A better understanding of how these catalysts are produced is crucial for the preparation of more effective catalysts in the future. The Revised Physical Adsorption (RPA) model simulates the uptake of Pt versus pH onto alumina but is simplistic in that only the doubly valent $[\text{PtCl}_6]^{2-}$ complex is considered. Because previous studies suggested that other Pt complexes might be present in the preparative solutions, investigators from the University of Illinois at Chicago, BP Research Center in Naperville, Illinois, and Argonne National Laboratory collaborated to refine the RPA model. By characterizing the molecular changes that occur when Pt complexes are adsorbed onto alumina, a better understanding of Pt adsorption is expected to lead to better control of the composition and performance of these catalysts.

The high sensitivity of the undulator beamline at MR-CAT, APS sector 10, was used to determine, via extended x-ray adsorption fine structure (EXAFS) measurements, the structures of Pt complexes in dilute solution and adsorbed on alumina. The exact structures of the aqueous Pt species were highly dependent on the Pt and Cl concentration, pH, and age of the solutions. For example, aqueous solutions of H_2PtCl_6 , which are commonly used to prepare catalysts, were observed to undergo rapid hydrolysis, giving Pt (IV) complexes with 3 Cl and 3 O ligands (Fig. 1). Although EXAFS cannot distinguish between OH and H_2O ligands, a proton balance indicated that the initial O ligands were H_2O . After about 24 h, as the solutions age, the H_2O ligands are exchanged by OH^- ions. The number of hydroxide ligands also increases as the pH increases.

In aqueous solution, γ -alumina with a surface area of about $200 \text{ m}^2/\text{g}$ becomes positively charged. A "double layer" theory is the kernel of the RPA model, which predicts that there is a Coulombic attraction between the negatively charged Pt complexes and the positive surface charge on alumina. Pt complexes, which initially contain H_2O ligands, are positively charged and not readily adsorbed. Aged solutions with hydroxide ligands, however, are readily adsorbed and lead to the formation of small particles upon reduction. EXAFS analysis (Fig. 1) also indicates that the Pt species undergo additional changes upon adsorption. These structural changes are due to the influence of the surface pH of the alumina. Proper control of the support, pH of the preparative solutions, and the charge on the metal complex, leads to monolayer coverage of the support and smaller metal particles upon reduction.

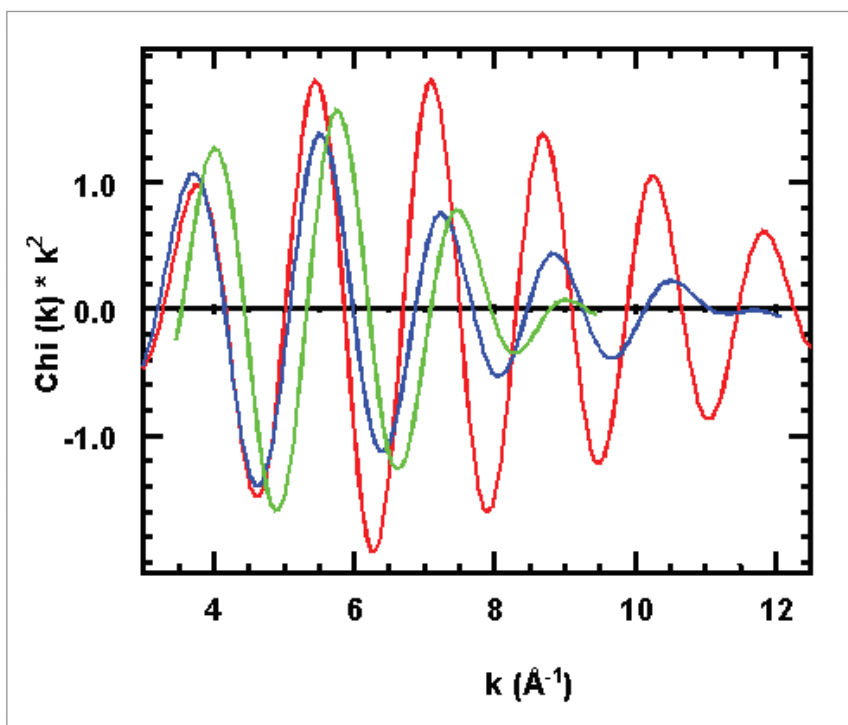


Fig. 1. k^2 -weighted EXAFS of solid H_2PtCl_6 (6 Pt-Cl at 2.32 \AA in red); 200 ppm H_2PtCl_6 at pH = 2.5 (2.7 Pt-Cl at 2.32 \AA and 3.3 Pt-O at 2.05 \AA) in blue; 200 ppm H_2PtCl_6 at pH = 2.5 adsorbed on alumina (1.7 Pt-Cl at 2.32 \AA and 4.3 Pt-O at 2.05 \AA) in green.

From this and similar studies, a general understanding has been developed that makes it possible to make superior catalysts with nearly any metal on any support. By using these advances, a simple method for production of a new generation of fuel cell electrodes, which has a very high Pt loading and very small metallic particles, has been recently developed. This work has attracted the interest of several catalyst manufacturers and is currently under development. ○

See: W.A. Spieker¹, J. Liu¹, X. Hao¹, J.T. Miller², A.J. Kropf³, and J.R. Regalbuto¹, "An EXAFS study of the coordination chemistry of hydrogen hexachloroplatinate (IV) 2. Speciation of complexes adsorbed onto alumina," *Appl. Catal. A* **243**, 53-66, (2003).

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